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<p>(54) Title: PHOTORESIST COMPOSITION CONTAINING A POLYMERIC ADDITIVE</p> <p>(57) Abstract</p> <p>A process for making a light-sensitive positive photoresist composition containing a film forming resin, a photoactive compound, a solvent, and a polymeric additive obtained by condensing a multihydroxyphenol and a ketone, where substantially all of the multihydroxyphenol, ketone, metal ion impurities and low molecular weight polymeric fraction have been removed from the polymeric additive. The photoresist of the instant invention improves the long term shelf stability of the photoresist solution and also provides good lithographic performance.</p> <p><i>methanol ethyl acetate</i></p>		

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DescriptionPhotoresist Composition Containing a Polymeric AdditiveBackground Of The Invention

5 Photoresist compositions are used in microlithography processes for making miniaturized electronic components such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The
10 coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

15 This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the coated surface of
20 the substrate.

25 There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating. Thereby uncovering a desired portion of the underlying substrate
30 surface on which the photoresist composition was deposited.

On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solution. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying substrate surface is uncovered.

After this development operation, the now partially unprotected substrate may be treated with a substrate-etchant solution or plasma gases and the like. The etchant solution or plasma gases etch that portion of the substrate where the photoresist coating was removed during development. The areas of the substrate where the photoresist coating still remains are protected and, thus, an etched pattern is created in the substrate material which corresponds to the photomask used for the image-wise exposure of the radiation. Later, the remaining areas of the photoresist coating may be removed during a stripping operation, leaving a clean etched substrate surface. In some instances, it is desirable to heat treat the remaining photoresist layer, after the development step and before the etching step, to increase its adhesion to the underlying substrate and its resistance to etching solutions.

Positive working photoresist compositions are currently favored over negative working resists because the former generally have better resolution capabilities and pattern transfer characteristics. Photoresist resolution is defined as the smallest feature which the resist composition can transfer from the photomask to the substrate with a high degree of image edge acuity after exposure and development. In many manufacturing applications today, resist resolution on the order of less than one micron are necessary. In addition, it is almost always desirable that the developed photoresist wall profiles be near vertical relative to the substrate. Such demarcations between developed and undeveloped areas of the resist coating translate into accurate pattern transfer

of the mask image onto the substrate. This becomes even more critical as the push toward miniaturization reduces the critical dimensions on the devices.

Positive-acting photoresists comprising novolak resins and quinone-diazide compounds as photoactive compounds are well known in the art. Novolak resins are typically produced by condensing formaldehyde and one or more multi-substituted phenols, in the presence of an acid catalyst, such as oxalic acid. Photoactive compounds are generally obtained by reacting multihydroxyphenolic compounds with naphthoquinone diazide acids or their derivatives.

Miniaturization of the semiconductor devices has lead to changes in the basic photoresist chemistries, in that resolution, photosensitivity, thermal stability have now become important factors that determine the choice of photoresist to be used in the processing of semiconductor devices. Higher resolution photoresists allow smaller dimensions to be delineated in the photoresist, photoresists with higher photosensitivity allow higher throughput of the substrates through the exposure step and photoresists with higher thermal stability allow for the use of higher processing temperatures for the photoresist without deforming the shape of the imaged photoresist.

Metal contamination has also been a problem for a long time in the fabrication of high density integrated circuits and computer chips, often leading to increased defects, yield losses, degradation and decreased performance. In plasma processes, metals such as sodium and iron, when they are present in photoresists, can cause contamination especially when silicon wafers are coated with a liquid positive photoresist and subsequently stripped off, such as with oxygen microwave plasma, the performance and stability of the semiconductor device is often seen to decrease. As the plasma stripping process is repeated, more degradation of the device frequently occurs. A primary cause of such problems has been found to be the metal contamination in the photoresist, particularly sodium and iron ions. Metal levels as low as 1.0 ppm in the photoresist have been found to adversely affect the properties of such semiconductor devices.

The present invention relates to the use of an additive in the photoresist that improves the performance of the photoresist as it relates to providing better resolution, higher photosensitivity, higher thermal stability, and additionally it has been unexpectedly found that removal of starting materials and any low molecular weight polymeric fractions from the additive greatly improves the long term stability of the photoresist solution. The additive that is incorporated in a photoresist is a polymer that is a condensation product of a multihydroxyphenol and a ketone, and from which starting materials, low molecular weight compounds, and metal ion impurities have been removed using a novel treatment process, to give a photoresist with significantly improved shelf stability and performance characteristics. The preferred combination of fractionating the additive and reducing the trace metal content makes the additive of this invention especially useful in photoresists.

Detailed Description Of The Invention

The present invention relates to photoresist compositions that comprise an additive that is obtained from the condensation of a phenolic compound that has more than one hydroxyl group and may have additional alkyl substituents, hereafter referred to as a multihydroxyphenol, and a ketone. The additive is preferably a purified product that contains no significant amounts of both the starting materials and low molecular weight fractions of the polymer. It has been observed that although the polymeric additive functions well in the photoresist composition even when the low molecular weight impurities are present, there is a tendency over long periods of time when the container with the photoresist remains unopened, for gasses to build up that lead to loss of shelf life stability. It was found unexpectedly that the removal of the starting materials and low molecular weight fraction from the additive resulted in a photoresist composition that did not degas and therefore had a longer shelf life than the photoresist composition with the untreated additive. The polymeric additive is additionally treated to remove metal ion impurities using a process that treats the ion exchange resins in a specific manner to obtain the most

efficient method for the removal of the metal ions from the additive. The polymeric additive may be synthesized using a process that eliminates these impurities or they may be removed after the synthesis and prior to addition into the photoresist. The present invention further provides a process for forming an image from a photoresist film from the composition of the present invention.

The production of film forming, novolak resins or polyvinylphenols, which may be used for preparing photosensitive compositions, are well known in the art. A procedure for the manufacture of novolak resins is described in Chemistry and Application of Phenolic Resins, Knop A. and Scheib, W.; Springer Verlag, N.Y., 1979 in Chapter 4 which is incorporated herein by reference. Paravinyl phenols and polyvinyl phenols are described in U.S. Pat. No. 3,869,292 and U.S. Pat. No. 4,439,516, which are incorporated herein by reference. Similarly, the use of o-diazonaphthoquinones as photoactive compounds is well known to the skilled artisan, as demonstrated by Light Sensitive Systems, Kosar, J.; John Wiley & Sons, N.Y., 1965 in Chapter 7.4, which is also incorporated herein by reference. These sensitizers which comprise a component of the present invention are preferably substituted diazonaphthoquinone sensitizers, which are conventionally used in the art in positive photoresist formulations. Useful photosensitizers include, but are not limited to, the sulfonic acid esters made by condensing phenolic compounds such as hydroxy benzophenones, oligomeric phenols and multisubstituted-multhihydroxyphenyl alkanes with naphthoquinone-(1,2)-diazide-5-sulfonyl chloride or naphtho-quinone-(1,2)-diazide-4-sulfonyl chlorides.

In photoresist technology, photoresists have finite shelf lives predicated on meeting consistent performance specifications over a defined period of time. Processing steps or modification of photoresists that increase the shelf life of a photoresist are important, in that, costly recalls or disposal of unsold materials can be minimized. It was found that if a polymeric additive which contained starting materials and low molecular weight polymer was added to the photoresist, then over a period of time gas was evolved in the unopened container and the shelf life of the photoresist was reduced. On the other hand,

when the impurities were removed from the additive in the photoresist, then degassing was significantly reduced and shelf life increased. Thus removal of the undesirable impurities in the photoresist became essential to prolonging the shelf life of the photoresist composition.

5 The polymeric additive of the invention is obtained from a condensation polymerization reaction of a multihydroxyphenol and a ketone. The multihydroxyphenol may contain two to three hydroxyl groups and additionally may also contain alkyl groups where the carbon chain length is between one to about four. The preferred multihydroxyphenol is pyrogallol, resorcinol or catechol. The most preferred multihydroxyphenol is pyrogallol. Ketones used
10 in the polymerization can be methyl ethyl ketone, acetone, _____

The preferred ketone is acetone. The polymerization uses an acid catalyst, for example, hydrochloric acid. After isolating the condensed product the starting materials and the low molecular weight fraction are removed. The preferred
15 molecular weight range of the removed low molecular weight fraction is that portion having a molecular weight average of less than 900 as measured using a gel permeation chromatograph. A preferred method is fractionation, although other methods, such as distillation or extraction may be used.

20 The polymeric additive is fractionated by adding a dilute solution of the polymeric additive, to a mixture of water, preferably deionized water, and an organic polar solvent. The additive solution is in a range of from about 5% to about 40% solids, more preferably from about 10% to about 30% and most preferably from about 15% to about 25% in solids. The solvent for the polymer solution can be a single solvent or a mixture of solvents. The single solvent
25 can be any of the solvents used as casting solvents for the photoresist, examples of which are propylene glycol mono-alkyl ether, propylene glycol alkyl (e.g. methyl) ether acetate, ethyl-3-ethoxypropionate, ethyl lactate, mixtures of ethyl-3-ethoxypropionate and ethyl lactate, 7-heptanone, 3-methoxy-3-methyl butanol, butyl acetate, xylene, diglyme, ethylene glycol monoethyl ether acetate. The preferred solvents are propylene glycol methyl
30 ether acetate (PGMEA), ethyl lactate, 7-heptanone ethyl-3-ethoxypropionate

(EEP) and 3-methoxy-3-methyl butanol. Alternatively, a mixture of solvents is used, where a polar organic solvent, such as acetone, methanol or ethanol, is added to the casting photoresist solvent. The amount of polar to nonpolar solvent can range from about 10:90 to about 90:10, preferably 25:75 to about 75:25 and more preferably 40:60 to 60:40. The aqueous fractionating solvent contains a polar organic solvent, such as acetone, methanol or ethanol. Preferably a mixture containing about 1% to about 30% methanol, more preferably from about 5% to about 20% methanol and most preferably from about 5% to about 15% methanol is used. In another embodiment only water, preferably deionized water, can be used providing an organic polar solvent is present in the mixture of solvents used to dissolve the additive. This fractionation is carried out under a constant temperature range of about 0° C to about 40° C, more preferably from about 5° C to about 30° C and most preferably from about 10° C to about 25° C. The resin precipitates out during the addition process, it is filtered, and washed with deionized water. The solid resin is dried to constant weight, preferably under vacuum and heat. The fractionation process may be repeated to further remove the low molecular weight fraction of the polymer. The desired process consists of fractionating 1-5 times, but more preferably 1-3 times. The efficacy of the fractionation can be monitored by measuring the reduction in the degassing rate of a photoresist made using the fractionated resin as compared to a resist made from the unfractionated resin.

The polymeric additive is additionally treated to remove the metal ion contaminants present. Methods that involve aqueous acid extraction or ion exchange may be used. In a preferred embodiment the polymeric additive solution is treated with a cation or an anion exchange resin that has been previously treated using a specific process. In a more preferred embodiment the additive is treated with both the cationic and anionic exchange resin that has been previously treated. In the most preferred embodiment the additive is filtered and treated with both the cationic and anionic exchange resins that have been previously treated.

The process of treating the ion exchange resin prior to removing the metal impurities is critical to this invention and to obtaining the maximum efficiency of metal ion removal. The process for treating the ion exchange resins comprises the following steps:

- 5 a) rinsing a cationic exchange resin with deionized (DI) water, followed by rinsing with a mineral acid solution (e.g. a 5-98% solution of sulfuric, nitric or hydrochloric acid), followed by rinsing again with DI water, and thereby reducing the level of sodium and iron ions in the cationic exchange resin to less than 200 ppb each, preferably less than 100 ppb,
10 more preferably less than 50 ppb and most preferably no more than 20 ppb; and
- b) rinsing an anionic ion exchange resin with DI water, followed by rinsing with a mineral acid solution (e.g. a 5-98% solution of sulfuric, nitric or hydrochloric acid), followed by rinsing again with DI water, then rinsing
15 with an electronic grade non-metallic (e.g. ammonium) hydroxide solution (normally a 4-28% solution), followed by rinsing again with DI water, and thereby reducing the level of sodium and iron ions in the anionic exchange resin to less than 200 ppb each, preferably less than 100 ppb, more preferably less than 50 ppb and most preferably no more
20 than 20 ppb.

It is critical that both these ion exchange resins are rinsed with a solvent which is the same as, or at least compatible with, the solvent of the additive, prior to metal ion removal. Cationic ion exchange resins such as those available from Rohm and Haas Company, e.g. AMBERLYST® 15, and anionic
25 exchange resin such as AMBERLYST® 21 can be used. Typically these resins as obtained contain unacceptably high levels of metal ions, as much as 80,000 to 200,000 ppb each of sodium and iron ions. Therefore an efficient treatment process for the ion exchange resins is critical before any metal ions can be removed from the additive.

30 The polymeric additive is dissolved in a non polar organic casting solvent, or in a mixture of a polar and a nonpolar organic casting solvent, and

5 passed through a filter, such as a 0.1 micron filter, through a cation exchange resin that has been treated in the manner described previously and also through a treated anion exchange resin also described previously. This treatment of the additive reduces the level of metal ion contaminants to less than 100 ppb, preferably less than 50 ppb and more preferably less than 25 ppb and most preferably less than 10 ppb. It was found that forming a solution of the additive, prior to the removal of metal ions, in a polar solvent such as methanol, ethanol, acetone or mixtures thereof, or in a mixture of a polar and nonpolar solvent, greatly facilitated the removal of metal ions.

10 The polymeric additive is preferably dissolved in a non polar solvent, such as any nonpolar solvent used as a casting solvent for the photoresist, and more preferably also contains a polar solvent such as methanol, ethanol and acetone in the solvent ratio of from about 1:2 to 2:1, preferably about 1:1, and with a resin solids content of from about 5 percent to about 30%, preferably from about 15% to about 25%. The resin solution may be passed through a column containing the ion exchange resins. Such resin solutions typically contain from about 250 to 1500 ppb each of sodium and iron ions. During the process of the present invention, these levels are reduced to levels as low as 10 ppb each.

20 The present invention provides a process for producing a photoresist compositions containing the polymeric additive of specific properties and a process for producing images using such photoresist compositions. The photoresist composition is formed by providing an admixture of a water insoluble, aqueous alkali soluble, film forming resin, a lightsensitive compound, the polymeric additive of the present invention and a suitable solvent. Suitable solvents for such photoresists and for the polymeric additive may include propylene glycol mono-alkyl ether, propylene glycol alkyl (e.g. methyl) ether acetate, ethyl-3-ethoxypropionate, ethyl lactate, mixtures of ethyl-3-ethoxypropionate and ethyl lactate, 7-heptanone, 3-methoxy-3-methyl butanol, butyl acetate, anisole, xylene, diglyme, ethylene glycol monoethyl ether acetate. The preferred solvents are propylene glycol methyl ether acetate

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(PGMEA), ethyl lactate, 7-heptanone, anisole, ethyl-3-ethoxypropionate (EEP) and 3-methoxy-3-methyl butanol.

The photoresist composition may additionally incorporate other alkali soluble water insoluble resins that have low levels of metal ions, such as polyhydroxystyrene, substituted polyhydroxystyrene, novolak resins made from mixtures of phenols and aldehydes, fractionated novolak resins, and other similar resins. It has been found that a particularly preferred composition comprises the polymeric additive of the present invention, fractionated novolak resin, photosensitive compound and a suitable solvent.

The photoresist composition is formed by blending the ingredients in a suitable solvent composition. In the preferred embodiment, the amount of novolak resin in the photoresist composition preferably ranges from 60% to about 95% and more preferably from about 70% to about 90% and most preferably from about 75% to about 85%, based on the weight of the total solid components of the resist.

In the preferred embodiment, the photosensitizer is present in the photoresist in an amount of from about 1% to about 35%, more preferably from about 5% to about 30% and most preferably from about 10% to about 20%, based on the weight of the solids components.

The polymeric additive of the present invention is added in a preferred range from about 1% to 30%, more preferably from about 5% to 25% and most preferably from about 5% to 20% based upon the solid components.

Other optional ingredients such as colorants, dyes, antistriation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers, solvents and such surfactants as nonionic surfactants may be added to the photoresist solution of the present invention before the solution is coated onto a substrate. Examples of dye additives that may be used together with the photoresist compositions of the present invention include Methyl Violet 2B (C.I. No. 42535), Crystal Violet (C.I. 42555), Malachite Green (C.I. No. 42000), Victoria Blue B (C.I. No. 44045) and Neutral Red (C.I. No. 50040) at one to ten percent weight levels, based on the combined weight of novolak resin and photosensitizer.

The dye additives help provide increased resolution by inhibiting back scattering of light off the substrate.

Anti-striation agents may be used at up to a five percent weight level, based on the combined weight of novolak resin and photosensitizer.

5 Plasticizers which may be used include, for example, phosphoric acid tri-(beta-chloroethyl)-ester; stearic acid; dicamphor; polypropylene; acetal resins; phenoxy resins; and alkyl resins at one to ten percent weight levels, based on the combined weight of novolak resin and photosensitizer. The plasticizer additives improve the coating properties of the material and enable the

10 application of a film that is smooth and of uniform thickness to the substrate.

Adhesion promoters which may be used include, for example, beta-(3,4-epoxy-cyclohexyl)-ethyltrimethoxysilane; p-methyl-disilane-methyl methacrylate; vinyltrichlorosilane; and gamma-amino-propyl triethoxysilane up to a 4 percent weight level, based on the combined weight of novolak resin and

15 photosensitizer. Development speed enhancers that may be used include, for example, picric acid, nicotinic acid or nitrocinnamic acid by a weight level of up to 20 percent, based on the combined weight of novolak resin and

photosensitizer. These enhancers tend to increase the solubility of the

20 photoresist coating in both the exposed and unexposed areas, and thus they

are used in applications when speed of development is the overriding

consideration even though some degree of contrast may be sacrificed; i.e., while the exposed areas of the photoresist coating will be dissolved more quickly by the developer, the speed enhancers will also cause a larger loss of photoresist coating from the unexposed areas.

25 The coating solvents may be present in the overall composition in an amount of up to 95% by weight of the solids in the composition. Solvents, of course are substantially removed after coating of the photoresist solution on a substrate and drying. Non-ionic surfactants that may be used include, for example, nonylphenoxy poly(ethyleneoxy) ethanol; octylphenoxy ethanol at up

30 to 10% weight levels, based on the combined weight of novolak resin and photosensitizer.

5 The prepared photoresist solution, can be applied to a substrate by any conventional method used in the photoresist art, including dipping, spraying, whirling and spin coating. When spin coating, for example, the photoresist solution can be adjusted with respect to the percentage of solids content in order to provide coating of the desired thickness given the type of spinning equipment utilized and the amount of time allowed for the spinning process. Suitable substrates include silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds. The photoresist coatings produced by the above described procedure are particularly suitable for application to thermally grown silicon/silicon dioxide-coated wafers such as are utilized in the production of microprocessors and other miniaturized integrated circuit components. An aluminum/aluminum oxide wafer can be used as well. The substrate may also comprise various polymeric resins especially transparent polymers such as polyesters. The substrate may have an adhesion promoted layer of a suitable composition such as one containing hexa-alkyl disilazane.

20 The photoresist composition solution is then coated onto the substrate, and the substrate is temperature treated at from about 80°C to about 110°C for from about 30 seconds to about 180 seconds on a hot plate or for from about 15 to about 40 minutes in a convection oven. This temperature treatment is selected in order to reduce the concentration of residual solvents in the photoresist while not causing substantial thermal degradation of the photosensitizer. In general one desires to minimize the concentration of solvents and thus this first temperature treatment is conducted until substantially all of the solvents have evaporated and a thin coating of photoresist composition, on the order of a micron in thickness, remains on the substrate. In a preferred embodiment the temperature is conducted at from about 85°C to about 95°C. The treatment is conducted until the rate of change of solvent removal becomes relatively insignificant. The temperature and time selection depends on the photoresist properties desired by the user as well as

equipment used and commercially desired coating times. The coating substrate can then be exposed to actinic radiation, especially ultraviolet radiation, at a wavelength of from about 300 nm to about 450 nm (preferably at about 365 nm), x-ray, electron beam, ion beam or laser radiation, in any desired pattern, produced by use of suitable masks, negatives, stencils, templates, etc.

The photoresist is then optionally subjected to a post exposure second baking or heat treatment either before or after development. The heating temperatures may range from about 90°C to about 150°C, more preferably from about 110°C to about 150°C. The heating may be conducted for from about 10 seconds to about 30 minutes, more preferably from about 45 seconds to about 90 seconds on a hot plate or about 10 to about 30 minutes by convection oven.

The exposed photoresist-coated substrates are developed to remove the imagewise exposed, non-image areas by spray developing using an alkaline developing solution. The solution is preferably agitated, for example, by nitrogen burst agitation. The substrates are allowed to remain in the developer until all, or substantially all, of the photoresist coating has dissolved from the exposed areas. Developers may include aqueous solutions of ammonium or alkali-metal hydroxides. One preferred hydroxide is tetramethyl ammonium hydroxide. A suitable developer is AZ Developer available commercially from the AZ Photoresist Products group of Hoechst Celanese Corporation, Somerville, New Jersey. After removal of the coated wafers from the developing solution, one may conduct an optional post-development heat treatment or bake in increase the coating's adhesion and chemical photoresistance to etching solutions and other substances. The post-development heat treatment can comprise the oven baking of the coating and substrate below the coating's softening point. The industrial applications, particularly in the manufacture of microcircuitry units on silicon/silicon dioxide-type substrates, the developed substrates may be treated with a buffered, hydrofluoric acid base etching solution. The photoresist compositions of the present invention are photoresistant to acid-base etching solutions and provide

- 14 -

effective protection for the unexposed photoresist-coating areas of the substrate.

The following specific examples will provide detailed illustrations of the methods of producing and utilizing the compositions of the present invention. These examples are not intended to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

Example 1

In a 1 liter round bottom flask fitted with stirrer and a thermometer with a constant temperature thermowatch unit, 183.3 g. of electronic grade acetone was mixed with 200 g of pyrogallol (1,2,3-trihydroxybenzene). The mixture was stirred for 15 minutes at room temperature to dissolve the solid pyrogallol. To this solution, 4.4 g of concentrated hydrochloric acid was added and the solution was gently heated to about 50°C, at which point a mild exotherm took the temperature up to about 77° C. Once the temperature leveled off, the thermowatch was set for a cut-off temperature of 90° C and heating was continued at reflux for 5 hours. The temp. ranged from 77°C to about 88°C during the course of the reaction. The reaction mixture became quite viscous with some large insolubles evident. 400 g of additional acetone was added to completely dissolve the resin and make the solution less viscous. The solution was refluxed for additional 2 hours. The solution was cooled to below 30° C and the resin was fractionated by drowning the acetone solution in 4000 ml. of deionized water over 1 hour period at 10° C.

The wet cake was split into 2 portions. The first portion was dried in a vacuum oven at 40° C overnight; the second portion of wet solids weighing 333 g was redissolved in 700 g of acetone. This solution was reprecipitated by drowning the acetone solution in 5 liters of deionized water over 1 hour period at 10°C. Gel permeation chromatographs (GPC) showed that the pyrogallol

and lower molecular weight (Mw) fractions were reduced progressively with each fractionation. The first fractionation increased the weight average Mw by about 3% while the second fractionation increased it by an additional 5.8%.

Example 2

Samples from several synthetic batches totaling 423.4 g were combined for the metal reduction procedure. These solids were dissolved in 635.1 g of ethyl lactate. The solution weighing 1058.5 g was diluted with 1058.5 g of acetone. Five hundred grams of this solution was drowned in a solution comprised of 3600 g of deionized water and 400 g of methanol at 15-20° C over 1 hour period. The solids isolated by filtration were washed with deionized water. After pulling vacuum through the filtered solids, 70 g of the wet solids were dissolved in 240 g of ethyl lactate. The solution was distilled under vacuum at about 30 mm. Hg and 80° C to remove residual water and concentrate the solution to about 35% solids. This solution was filtered through a 0.2 μ filter and then sequentially passed through a treated cationic ion exchange bed (Rohm & Haas A15) followed by a treated anionic bed (Rohm & Haas A21) keeping the dwell time in each bed at 12-15 minutes. The metal reduction data is given in Table 1.

Table 1 Metal ion Test Results

<u>Metal</u>	<u>Before Treatment</u>	<u>After Treatment</u>
Na	78	8
K	81	2
Fe	739	2
Cr	64	2
Cu	24	<1
Ni	38	2
Ca	462	12
Al	374	1

- 16 -

Gel Permeation Chromatography showed that the fractionated resin had almost no unreacted pyrogallol, acetone or lower molecular weight fraction relative to the unfractionated resin. A photoresist solution was made using 15.6% novolak resin, 6.1 g of the treated acetone-pyrogallol resin, 6.7%
5 photoactive compound made from condensing a para-cresol/formaldehyde copolymer with 2,1,5 diazonaphthoquinone sulfonate, where about 35% of the phenolic hydroxy groups were esterified. A comparative photoresist solution was made using the above formulation except the untreated acetone-pyrogallol resin was used.

10 A comparison of degassing rates of resists showed about a 30-40% reduction in the degassing rate for the resist made with the treated resin. These degassing rates were monitored by noting the pressure increase in sealed stainless steel tubes fitted with calibrated pressure gauges submerged in a water bath thermostatted at 50° C and calculating the slopes of the straight
15 line portion of the time/ln pressure graphs.

Example 3

250 g of unfractionated pyrogallol-acetone resin in ethyl lactate (40% solids) was diluted with 262.5 g of acetone. This was added over about a 2 1/2
20 hour period to a solution comprised of 256.2 g of methanol and 2306.3 g of deionized water. The resulting solids were gummy. These were vigorously agitated with a high shear blender with an additional 2500g of deionized water. The solids were filtered air dried and then dried in a vacuum oven (~24 in. H₂O) overnight at 40°C. A 41% solids solution of the resin was made by dissolving
25 78.9g of the dried solids in 113.5g of ethyl lactate.

Two photoresists were prepared as follows:

To each of two separate mixing vessels, 585.3 g of a 41% solids solution of a novolak resin comprised of the reaction product of a 45/55 meta/para
30 cresol: formaldehyde was mixed with 86.3 g of the reaction product of 2,1,5 diazonaphthoquinone sulfonyl chloride with an oligomer of p-cresol formaldehyde resin (6-8 repeat units), where approximately 35% of the

phenolic hydroxy groups are converted to the sulfonate esters. The solutions were further diluted with 147.6g of ethyl lactate. To resist solution A, 180 g of the unfractionated resin in ethyl lactate solution was added while 180 g of the 41% solids solution from the above mentioned fractionated resin was added to resist solution B.

The photoresists were compared for their degassing behavior. The control sample A showed about a 30-40% faster degassing rate than resist B made with the fractionated resin. These degassing rates were monitored by noting the pressure increase in sealed stainless steel tubes fitted with pressure gauges where the tubes were heated to 50°C in a constant temperature bath. In all other respects the unaged resists had comparable lithographic properties.

Example 4

A speed enhancing resin was prepared by reacting 1 mole of resorcinol (1,3-dihydroxybenzene) with 2 moles of acetone using 0.12 moles of hydrochloric acid as a catalyst for about 4 hours. The reaction mixture became very viscous with some evidence of insolubles. Ethyl lactate was added and the mixture was heated to make a solution. Excess acetone and water of reaction were distilled off at elevated temperature under vacuum. Solids were adjusted to approximately 40%. The ethyl lactate solution of the resin was used to prepare resist solution with the same component ratios as noted in Example 1. The resist had comparable properties to that of Example 1 except for about 10-20% reduced photospeed.

Example 5

100 g of pyrogallol and 90.5 g of acetone was taken in a 1000 ml round bottom flask equipped with condenser, thermometer and stirring. 2.2 g of 36% hydrochloric acid was added heated to 40°C, the exotherm reaction was started and temperature went up to 88°C. The reaction was allowed to run for five hours when the reaction mixture turned to viscous. 70 g of acetone was added and the reaction was continued for two more hours. The reaction mixture was

- 18 -

cooled down to room temperature and was transferred to a dropping funnel. The mixture was added to water at 10°C from the dropping funnel on stirring. The crystals aware redissolved in 300 g acetone and the solution was dropped to 2500 ml water. The crystals were filtered and dried in a vacuum drier. Metal
5 ions were analyzed and found to be Na 45 ppb, Fe 239 ppb, and Ca 236 ppb. The resin can be further treated to reduce the trace metals and formulated into a photoresist.

Example 6

10 100 g of pyrogallol and 90.5 g of acetone was taken in a 1000 ml round bottom flask equipped with condenser, thermometer and stirring. 2.2 g of 36% hydrochloric acid was added heated to 40°C, the exotherm reaction was started and temperature went up to 88°C. The reaction was allowed to run for five hours when the reaction mixture turns to viscous. 70 g of acetone was added
15 and the reaction was continued for two more hours. The reaction mixture was cooled down to room temperature and water was added from a dropping funnel on stirring. The stirring was stopped and the precipitate was allowed to settle. The liquid phase was removed from the top. The precipitate was redissolved in 300 g of acetone and deionized water was added slowly to form a precipitate.
20 The liquid phase was removed from the top and ethyl lactate was added to dissolve the precipitate. The residual water and acetone were distilled off to yield the resin in ethyl lactate. A sample was analyzed for metal ions and found to be Na 140 ppb, Fe 27 ppb, and Ca 16 ppb.

Example 7

25 55 grams of dry AMBERLYST®15 ion exchange resin beads were placed in a conical flask and deionized water was added so that all of the resin beads were under water. The flask was sealed and allowed to stand overnight to swell the resin beads. The next morning the water was decanted, deionized
30 water was added to cover the resin beads and the flask was shaken slowly. The water was again decanted. The rinsing with deionized water and

decanting steps were repeated three additional times. The resulting slurry of anion exchange resin was poured into a glass column equipped with a porous disk and a stopcock. The resin was allowed to settle to the bottom and the column was back flushed with deionized water for 25 minutes. The resin was again allowed to settle to the bottom.

The bed length was measured and the bed volume was found to be 100 ml. A 10 percent sulfuric acid solution was passed down through the resin bed at a rate of about 10 ml./min. 6 bed volumes of the acid solution were passed down through the resin bed. 60 bed volumes of deionized water were then passed down through the resin bed at about the same flow rate. The pH of the effluent water was measured to assure that it matched the pH of 6.0 for fresh deionized water. Two bed volumes of electronic grade methanol were passed down through the column to remove the water.

80 grams of wet Amberlyst®21 anion exchange resin beads were placed in a conical flask and deionized water was added so that all of the resin beads were under water. The flask was sealed and allowed to stand overnight to swell the resin beads. The next morning the water was decanted, more deionized water added to cover the resin beads and the flask was shaken slowly. The water was again decanted. The rinsing with deionized water and decanting steps were repeated three additional times. The resulting slurry of anion exchange resin was poured into a glass column having a diameter equipped with a porous disk and a stopcock. The resin was allowed to settle to the bottom and the column was back flushed with deionized water for 25 minutes. The resin was again allowed to settle to the bottom.

The bed length was measured and the bed volume was calculated as 125 ml. A 10 percent sulfuric acid solution was passed down through the resin bed at a rate of about 10 ml./min. 6 bed volumes of the acid solution were passed through the resin bed. An amount of deionized water sufficient to remove the acid was then passed down through the resin bed at about the same flow rate. Six bed volumes of a 6 percent ammonium hydroxide solution was passed down through the column at the same rate, followed by about 60

- 20 -

bed volumes of DI water to remove ammonium hydroxide. The pH of the effluent water was measured to assure that it matched the pH of 6.0 for fresh deionized water. 2 bed volumes of electronic grade methanol was passed down through the column to remove water.

5 250 g of pyrogallol and acetone condensed resin in ethyl lactate (30% solution) from Example 6 was passed through a 0.1 μm (micrometer) filter through a cleaned and rinsed Amberlyst®15 ion exchange resin bed as above, followed by passage through a cleaned and treated Amberlyst®21 ion exchange resin bed as above, with a residence time of 12-15 minutes. Metal
10 analysis result before and after treatment are shown in Table 2.

Table 2 Results of Metal Testing

<u>Metals</u>	<u>Before (ppb)</u>	<u>After Filter(ppb)</u>	<u>After A-15 (ppb)</u>	<u>After A-21 (ppb)</u>
Na	65	85	6	2
Fe	29	7	9	5
K	28	21	2	1
Cr	2	6	1	<1
Cu	2	5	<1	<1
Ca	43	23	<1	<1
Al	40	5	1	<1
Mn	2	3	2	2
Ni	<1	<1	<1	<1

Claims

1. A process for producing a photoresist composition comprising the steps of:
 - a) providing a polymer obtained by condensing a multihydroxyphenol with a ketone using an acid catalyst;
 - b) removing residual multihydroxyphenol, ketone and low molecular weight fraction of the polymer;
 - c) removing metal ion impurities;
 - d) adding the purified polymer to an admixture comprising a film forming resin, a lightsensitive compound, and an organic solvent.
2. The process according to claim 1, wherein the multihydroxyphenol is resorcinol.
3. The process according to claim 1, wherein the multihydroxyphenol is pyrogallol.
4. The process according to claim 1, wherein the ketone is acetone.
5. The process according to claim 1, wherein the acid catalyst is hydrochloric acid.
6. The process according to claim 1, wherein fractionation is used for substantially removing residual multihydroxyphenol, ketone or low molecular weight fraction of the polymer.
7. The process according to claim 6, wherein a mixture of an organic polar and an organic nonpolar solvent is used for dissolving the polymer and the polymer solution is further fractionated from a mixture of water and an organic polar solvent between a temperature of about 0°C to about 40°C.

8. The process according to claim 6, wherein a mixture of an organic polar and an organic nonpolar solvent is used for dissolving the polymer and the polymer solution is further fractionated from water between a temperature of about 0°C to about 40°C.

9. The process according to claim 6, wherein an organic nonpolar solvent is used for dissolving the polymer and the polymer solution is further fractionated from a mixture of water and an organic polar solvent between a temperature of about 0°C to about 40°C.

10. The process according to claim 1, wherein distillation is used for substantially removing residual multihydroxyphenol or ketone.

11. The process according to claim 1, wherein removing the metal ion impurities comprises the steps of:

- a) washing an anion exchange resin with deionized water, washing said anion exchange resin with a mineral acid solution, washing said anion exchange resin again with deionized water, washing said anion exchange resin with ammonium hydroxide, washing said anion exchange resin with deionized water again, and thereby reducing the level of sodium and iron ions in said anion exchange resin to less than 200 ppb each;
- b) washing a cation exchange resin with deionized water, washing said cation exchange resin with a mineral acid solution, washing said cation exchange resin with deionized water and thereby reducing the level of sodium and iron ions in said cation exchange resin to less than 200 ppb each;
- c) providing a solution of the polymer in an organic solvent, passing said solution through a filter having a pore size of from 0.04 to 0.5 microns, passing said solution through said treated cationic and

anionic exchange resins and thereby reducing the level of sodium and iron ions in said solution to less than 200 ppb each.

12. The process according to claim 11, wherein the polymer is in a solution of an organic nonpolar solvent and an organic polar solvent.
13. The process according to claim 1, wherein aqueous acid extraction is used for removing the metal ions.
14. The process according to claim 1, wherein the level of metal ions is less than 50 ppb each ion.
15. The process according to claim 1, wherein the polymer is present in the photoresist composition at about 1% to about 30% by weight of the total photoresist.
16. The photoresist composition according to claim 1, wherein the photoactive compound is a reaction product of a diazonaphthoquinone sulfonyl residue and a phenolic residue.
17. The photoresist composition according to claim 16, wherein the phenolic residue is selected from a group consisting of multihydroxybenzophenones, multihydroxyphenylalkanes, phenolic oligomers, and mixtures thereof.
18. The photoresist composition according to claim 16, wherein the naphthoquinone sulfonyl residue is selected from a group consisting of 2,1,4-diazonaphthoquinone sulfonyl, 2,1,5-diazonaphthoquinone sulfonyl, or mixtures thereof.
19. The photoresist composition according to claim 1, wherein the resin is a novolak resin.

20. The photoresist composition according to claim 19, wherein the novolak resin is an acid catalysed condensation product of an aldehyde and one or more substituted phenolic monomers.

21. The photoresist composition according to claim 1, wherein the resin is polyhydroxystyrene.

22. The photoresist composition according to claim 1, wherein the resin is substituted polyhydroxystyrene.

23. The photoresist composition according to claim 1, wherein the organic solvent is selected from a group consisting of propylene glycol mono-alkyl ether, propylene glycol methyl ether acetate, 2-heptanone, butyl acetate, anisole, amyl acetate, ethyl-3-ethoxypropionate, ethyl lactate, ethylene glycol monoethyl ether acetate, ethyl lactate, and mixtures thereof.

24. The composition of claim 1, further comprising one or more additives selected from a group consisting of colorants, leveling agents, anti-striation agents, plasticizers, adhesion promoters, speed enhancers and surfactants.

25. A process for imaging photoresist comprising the steps of:

- a) coating a substrate with a positive photoresist composition from claim 1;
- b) heat treating the coated substrate until substantially all of said solvent composition is removed;
- c) imagewise exposing the coated photoresist composition to actinic radiation;
- d) removing the imagewise exposed areas of said coated photoresist composition with a developer; and

- e) optionally, heating the substrate either before or after the removing step.
26. The method of claim 24, further comprising heating said coated substrate from a temperature of from about 90°C to about 150°C for from about 30 seconds to about 180 seconds on a hot plate or from about 15 minutes to about 40 minutes in an oven after the exposure step but before the developing step.
27. The method of claim 24, further comprising heating said coated substrate at a temperature of from about 90°C to about 150°C for about 30 second to about 180 seconds on a hot plate or for from about 15 minutes to about 40 minutes in an oven after the developing step.
28. The method of claim 24, wherein the exposure step is conducted with radiation having a wavelength from about 180 nm to about 450 nm.
29. The method of claim 24, wherein the developer is an aqueous alkaline solution.
30. The method of claim 24, wherein the developer is an aqueous solution of tetramethylammonium hydroxide.

INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/EP 97/07052

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/023

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 360 692 A (KAWABE YASUMASA ET AL) 1 November 1994 see column 9, line 29 - line 32 ---	1-30
A	EP 0 358 871 A (SUMITOMO CHEMICAL CO) 21 March 1990 see page 5, line 54 - page 6, line 6 see page 6, line 40 - line 43 ---	1-30
A	EP 0 251 187 A (NIPPON ZEON CO ;FUJITSU LTD (JP)) 7 January 1988 see claims ---	1-30
A	EP 0 477 691 A (FUJI PHOTO FILM CO LTD) 1 April 1992 see page 4, line 4 - line 8 see page 8, line 47 - line 53 ---	1-30
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter. Jnal Application No

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